

# The worm turned, and the ocean followed

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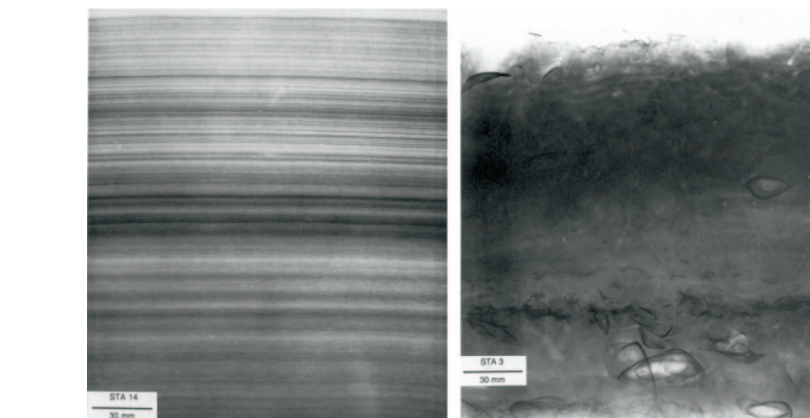
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Unless you hang drywall or travel in certain biogeochemical circles, the calcium sulfate mineral gypsum is probably not on your radar—nor is the amount of sulfate ( $\text{SO}_4^{2-}$ ) dissolved in seawater, which determines how much gypsum is left behind when that seawater evaporates. All the same, sulfate is the second most abundant negatively charged ion dissolved in seawater today, and tracking its changing concentration in the ocean over the earth's 4.5-billion-year history is one of a geochemist's best windows to the chemical and biological evolution of the early ocean and atmosphere. Now, in a novel slant on the sulfate tracer, Canfield and Farquhar in this issue of PNAS (1) link dramatic increases in seawater sulfate in the early Paleozoic Era, 540–460 million years ago, to a major biological innovation: the invasion of marine sediments by burrowing, mud-churning organisms (Fig. 1). And the net result, the authors argue, was the world's first massive deposits of gypsum.

The premise of Canfield and Farquhar's isotope-driven numerical model for sulfate and gypsum abundance through time hangs on the simple observation that gypsum first became plentiful at roughly the same time as the first appearance of burrowing organisms. Gypsum forms in arid, restricted settings where evaporation drives up the concentrations of dissolved sulfate and calcium to the levels required for its precipitation, and the higher the initial concentration of sulfate, the more likely this process will occur. It is certain that sulfate delivery to the ocean increased over time, and consequently its concentration, but this overall rise was dampened by the formation in the ocean of another mineral, pyrite.

At the other end of the sulfur cycle, the origin of most seawater sulfate is tied to the chemical breakdown of pyrite exposed on the continents under an atmosphere containing at least a modest amount of oxygen, followed by transport to the ocean by rivers. This delivery began in earnest about 2.4 billion years ago as oxygen first accumulated beyond the trace amounts present in the earliest atmosphere. Evidence for this "Great Oxidation Event" (GOE) and the corresponding increase in sulfate delivery to the ocean comes in many forms, including distributions of the isotopes of sulfur preserved in pyrite found in ancient sedimentary rocks.

Pyrite formation begins when bacteria convert sulfate to hydrogen sulfide ( $\text{H}_2\text{S}$ ) as they metabolize organic matter. In doing so, the microbes typically show a



**Fig. 1.** X-ray images of two sediment cores from the modern Black Sea. Sediments from the oxygen-free deep basin (*Left*) show undisturbed annual, submillimeter-scale layers (varves) preserved in the complete absence of animals on or below the seafloor. Those from the oxic shallow shelf (*Right*), by contrast, reveal nearly complete homogenization, with an active burrow layer extending at least 10 cm below the seafloor. Discrete burrows are visible in the X-ray. Only shell layers formed by storm reworking have been spared complete disruption. These extreme end members in degrees of bioturbation are much like the transition in earth history from no to pervasive sediment mixing described by Canfield and Farquhar (1). Shallow burrowers incapable of intense sediment mixing and sulfur oxidation characterized the time interval bridging these extremes. The first rigorous mixing of sediments by animals, in the early to mid Paleozoic, was a consequence in part of increased oxygen availability. (Scale bars, 3 cm.)

strong preference for the light isotope ( $^{32}\text{S}$ ) relative to heavier and less abundant  $^{34}\text{S}$ . This discrimination, or fractionation, becomes muted during severe sulfate shortages—that is, when its concentration is less than about 1% of that in the modern ocean. The lack of isotopic fractionation in pyrite that formed more than 2.4 billion years ago reinforces the assumption that sulfate concentrations below this low threshold prevailed in the absence of abundant oxidative weathering on the continents (2).

Not only does pyrite formation provide an estimate of the sulfate concentration of early seawater, but that process and gypsum precipitation are the two principal pathways by which sulfate is removed from the ocean. When the  $\text{H}_2\text{S}$  reacts with iron to form pyrite, sulfate is lost from seawater, as long as the pyrite is buried and not reoxidized back to sulfate. Pyrite forms under oxygen-free local conditions, and for a variety of reasons its formation, preservation, and burial are favored in oxygen-poor settings such as the modern Black Sea, where oxygen is absent in all but the shallowest parts of the water column.

There is reason to believe that oxygen deficiencies may have persisted in the deep ocean for 1–2 billion years after the GOE (3, 4). There is also ample evidence for comparatively low sulfate concentrations in the ocean, perhaps only about

10% of today's, over much of this interval (5)—just as we would expect from a high rate of pyrite burial. Among the principal evidence for low seawater sulfate is the sparse record of gypsum deposition during this interval.

Gypsum is a soluble salt, and so its preservation at the earth's surface over long periods is favored only under the driest conditions. But the paucity of early gypsum is certain to reflect more than preservational bias. Instead, we can imagine how difficult it was in a low-sulfate ocean to reach the elevated concentrations of sulfate needed to permit gypsum precipitation during evaporation, as Canfield and Farquhar argue (1). Gypsum did precipitate in the ocean during the Proterozoic spanning from about 2.5 billion to 540 million years ago (6, 7), but Canfield and Farquhar assert that abundant gypsum was rare before the early parts of the Paleozoic. Their new model mitigates the impact of preservational skewing by predicting gypsum precipitation over time from isotope mass balance relationships.

If we imagine more than a billion years of pyrite burial under the low-oxygen,

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sulfide-rich conditions in the deep Proterozoic ocean, it is not a stretch to also imagine that sulfate concentrations were low throughout that eon, including its later portions (8). Only through subsequent oxygenation of the deep ocean and the resulting decrease in pyrite burial did sulfate increase in the Paleozoic to concentrations that could support gypsum precipitation on a large scale (9–11). At the same time oxygen increased in the deep ocean, its concentrations may have increased in the surface ocean and atmosphere to the point of ushering in the first animals.

But Canfield and Farquhar (1) take the story a step further. They contend that the key development was the introduction of animals, more specifically those first living within rather than on the surface of marine sediments, whose activity favored sulfide reoxidation to sulfate over its burial as pyrite. Burrowing animals, as they build dwellings and forage for food, influence the redox state of sediments in a number of ways. Principal among these impacts are physical mixing, or bioturbation, and pumping of seawater into the subsurface through a process known as bioirrigation. Given the ubiquity of strong burrowing, only a tiny fraction ( $\approx 5\%$ ) of the hydrogen sulfide produced in sediments today escapes reaction with oxygen and becomes buried as pyrite. In the absence of this biological activity, however, the efficiency of pyrite burial would have been much higher, just as it is in the deep Black Sea today, and the amount of pyrite burial would be limited only by the availability of reactive iron.

The stirring and irrigation of sediments by early animals would have exposed deeper oxygen-free, sulfide-rich sediments to the oxygen from the overlying seawater. This effect is particularly pronounced when the intensity and depth of burrowing vary seasonally, so that frequent temporal shifts occur from anoxic and oxic conditions, and earlier-formed hydrogen sulfide and pyrite are oxidized in the process (12). The net result is that less of the hydrogen sulfide is stored as pyrite, sulfate is returned to pore waters of the sediment and overlying seawater, and concentrations of sulfate in both settings are higher than those expected with effi-

cient pyrite burial. The likelihood of achieving the high sulfate concentrations necessary for gypsum precipitation rises correspondingly.

This relationship between sulfur recycling and the attendant decrease in pyrite burial efficiency and increases in sulfate concentration and gypsum precipitation must have been among the important geochemical responses to the biological innovation of burrowing, but just how important is a matter of debate. The latest Proterozoic ( $\approx 550$  million years ago) is known for massive gypsum deposits (7), and pockets of early seawater trapped in the mineral halite (NaCl) (13) also suggest high sulfate levels even when burrowing was insufficient to achieve the recycling effects invoked by Canfield and Farquhar (1). The authors note this contradiction in their numerical and conceptual models. And early Paleozoic sulfate concentrations were probably low even after the bioturbation was well established (9–11). If low sulfate levels persisted or returned in the early Paleozoic, either the overall impact of strong sulfur recycling is exaggerated or the capacity of early burrowing to facilitate this recycling via reoxidation was less intense than Canfield and Farquhar describe.

As the authors acknowledge, the earliest sediment dwellers may not have been efficient mixers of solids and fluids (14). Consistent with this possibility, their model does predict increased gypsum deposition coincident with the later invigoration of these processes. By some estimates, however, sulfate concentrations remained only a small fraction of those predicted by the model of Canfield and Farquhar (1) even after this intensification of burrowing (9–11). There remains the need to validate the model by bettering and expanding imperfect and sometimes inconsistent, independent estimates of sulfate concentrations, such as the inclusions in halite. Also, it is critical to remember that deposition of gypsum and other evaporite minerals is favored by volume loss during evaporation, such that some gypsum formation can occur even when the initial sulfate concentration was extremely low—as during intervals well before the GOE 2.4 billion years ago (15). As such, climate, along with tectonic controls on

the exchange of seawater between the open ocean and the site of gypsum deposition, remain important factors.

Perhaps the biggest question is whether the advent of burrowing and efficient sulfur cycling simply shifted the locus of pyrite burial from the upper layers to the sediments below the deepest extent of burrowing, typically only a few tens of centimeters or less. Given adequate organic matter, sulfate reduction would continue at depth, yielding pyrite that was invulnerable to the reoxidation effects perpetrated by burrowing. Canfield and Farquhar might respond by suggesting that burrowing organisms' frequent and pervasive reworking of the surface sediments would burn through much of the organic matter that would otherwise be readily and necessarily degraded by hydrogen sulfide-generating, sulfate-reducing bacteria if delivered below the mixed surface layer.

In a complex early world marked by an evolving ocean-atmosphere system taking big, first-order steps in its properties, it is always dangerous to invoke single controls on major chemical transitions. Canfield and Farquhar would be the first to admit this risk. They might even agree that sulfate concentrations increased in the later ocean, in a general sense, because of thorough oxygenation of the deep ocean for the first time and the related increase in oxygen levels in the shallow ocean. Pyrite burial would decrease under such conditions for a variety of reasons, with expanded bioturbation being only one of the factors.

In this sense the appearance of animals and their invasion of the muddy seafloor may coincide with growing levels of sulfate in the ocean because both are responding to the increasingly oxidizing milieu of the surficial biosphere—and not principally because the former is driving the latter. The animals may have first moved underground, at least in part, because more oxygen was available to support subsurface dwelling. But any way you slice it, all these effects are linked, and the downward movement of animals and the concomitant impact on biogeochemical cycling must have made a difference in the evolving chemistry of the ocean.

1. Canfield DE, Farquhar J (2009) Animal evolution, bioturbation, and the sulfate concentration of the oceans. *Proc Natl Acad Sci USA* 106:8123–8127.
2. Habicht K, Gade M, Thamdrup B, Berg P, Canfield DE (2002) Calibration of sulfate levels in the Archean ocean. *Science* 298:2372–2374.
3. Canfield DE (1998) A new model for Proterozoic ocean chemistry. *Nature* 396:250–253.
4. Scott C, Lyons TW, Bekker A, Shen Y, Poulton SW (2008) Tracing the stepwise oxygenation of the Proterozoic ocean. *Nature* 452:456–460.
5. Kah LC, Lyons TW, Frank TD (2004) Low marine sulphate and protracted oxygenation of the Proterozoic biosphere. *Nature* 431:834–838.
6. Melezhik V, et al. (2005) Emergence of an aerobic biosphere during the Archean-Proterozoic transition: Challenges of future research. *GSA Today* 15:4–11.

7. Mattes BW, Conway Morris S (1990) Carbonate/evaporite deposition in the Late Precambrian-Early Cambrian Ara Formation of southern Oman. *The Geology and Tectonics of the Oman Region*, eds Robertson AHF, Searle MP, Ries AC (Geol Soc, London), Special Publication 49, pp 617–636.
8. Canfield DE, et al. (2008) Ferruginous conditions dominated later Neoproterozoic deep-water chemistry. *Science* 321:949–952.
9. Canfield DE (2004) The evolution of the Earth surface sulfur reservoir. *Am J Sci* 304:839–861.
10. Gill BC, Lyons TW, Saltzman MR (2007) Parallel, high-resolution carbon and sulfur isotope records of the evolving Paleozoic marine sulfur reservoir. *Palaeogeog Palaeoclimat Palaeoecol* 256:156–173.
11. Horita J, Zimmermann H, Holland HD (2002) Chemical evolution of seawater during the Phanerozoic: Implications from the record of marine evaporates. *Geochim*

*Cosmochim Acta* 66:3733–3756.

12. Aller RC (1980) Diagenetic processes near the sediment-water interface of Long Island Sound. II. Fe and Mn. *Estuarine Physics and Chemistry: Studies in Long Island Sound*, ed Saltzman B. *Advances in Geophysics* (Academic, New York), Vol 22, pp 351–415.
13. Brennan ST, Lowenstein TK, Horita J (2004) Seawater chemistry and the advent of biocalcification. *Geology* 32:473–476.
14. Droser ML, Jensen S, Gehling JG (2002) Trace fossils and substrates of the terminal Proterozoic–Cambrian transition: Implications for the record of early bilaterians and sediment mixing. *Proc Natl Acad Sci USA* 99:12572–12576.
15. Buick R, Dunlop JSR (1990) Evaporitic sediments of Early Archaean age from the Warrawoona Group, North Pole, Western Australia. *Sedimentology* 37:247–277.